

RENEWABLE HYDROGEN PRODUCTION BY CATALYTIC STEAM REFORMING OF PEANUT SHELLS PYROLYSIS PRODUCTS

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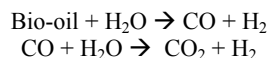
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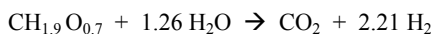
Introduction

The goal of this work is the production of renewable hydrogen from agricultural residues, in the near-term time frame and at a comparable cost to existing methane-reforming technologies. Near term production of renewable hydrogen from biomass requires a co-product strategy to compete with conventional production of hydrogen from the steam reforming of natural gas.^{1,2} The production of hydrogen by the processing of pyrolysis products that are produced as a by-product of activated carbon is one path that is possible to demonstrate the co-product strategy.

NREL began the development of a biomass to hydrogen process in 1993.¹ The original concept was that the pyrolysis oil could be fractionated into two fractions based on water solubility. The water-soluble fraction is to be used for hydrogen production and the water insoluble fraction could be used in adhesive formulations.³ The bio-oil can be stored and shipped to a centralized facility where it is converted to hydrogen via catalytic steam reforming and shift conversion. Catalytic steam reforming of Bio-oil at 750-850°C over a nickel-based catalyst is a two-step process that includes the shift reaction:



The overall stoichiometry gives a maximum yield of 17.2 g H/100 g bio-oil (a 40-50% energy yield is expected in practice):



The process has been demonstrated at the bench scale using model compounds and the carbohydrate-derived fraction of bio-oil.^{1,4} Regional networks of pyrolysis plants could be established to provide oil to a central steam reforming facility. The process is adaptable to other organic waste streams such as aqueous-steam fractionation processes used for ethanol production and trap grease. Recent laboratory work has demonstrated the feedstock flexibility with the processing of pyrolysis oil fractions from different feedstocks as well as other biomass-derived streams such as glycerine from biodiesel production, trap grease, and wood hydrolysis effluents.⁵

Although the adhesive byproduct option remains viable, commercial deployment opportunities are still not near term. Hence, other opportunities had to be developed based on the co-product strategy. The conversion of biomass to activated carbon is an alternative route to hydrogen with a valuable co-product as outlined in Figure 1. Slow pyrolysis is used in the first step of the activated carbon process to maximize the yield of charcoal and organic vapors are produced as a by-product in 25% yield. Southwest Georgia was identified as an excellent opportunity because of the importance of agriculture, the forest product industry and the need for zero emission transportation fuels in the Atlanta area. Scientific Carbons Inc. in Blakely GA uses pelletized peanut shells as the feed material for the production of activated carbon. They feed up to 1000 kg/hour of the densified peanut shells to a two-stage process producing activated carbon. The vapor by-products from the first stage, pyrolysis, are currently used as fuel for steam generator.

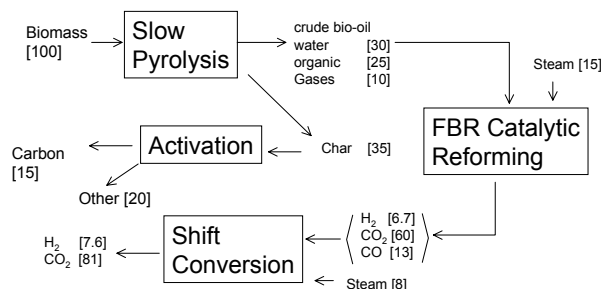


Figure 1. Mass Balance and Unit Operations in the Slow Pyrolysis of Biomass to Activated Carbon and Hydrogen

Catalyst performance is promising with run times in a two-inch fluid bed reactor of over 100 hours. Systematic studies of variation in catalyst composition have shown that commercial steam reforming catalysts perform well for the conversion.⁶ However, physical attrition is a problem since these catalysts are not manufactured for fluid bed operation.⁴

This paper reports on the design, set up, and shake-down of the scaled-up catalytic steam reforming reactor and on the initial tests for conversion of whole biomass pyrolysis vapors to hydrogen.

Experimental

Pelletized peanut shells obtained from the Birdsong peanut processing plant in Blakely, GA, were fed to a 20 cm fluid bed pyrolysis reactor. An in-line grinder was used to reduce the particle size to that required for fluid bed operation. Superheated steam at a mass ratio of 1.5:1 was used as a carrier gas and also as a reactant in the reformer. 10 kg/hour of pelletized peanut shells were fed into a bed of 300-400 μm sand at 500 °C. Char is separated in two cyclones. The steam/vapor stream then enters a preheater that raises its temperature to 650-700°C.

The catalytic fluid bed reformer can process 7-10 kg/h of pyrolysis vapor. The maximum allowable operating temperature and pressure are 900 °C and 140 kPa, respectively. The reformer is equipped with fluid bed reactor, vapor and liquid injection, steam and O₂ injection, internal and external cyclones for disengaging catalyst particles, instrumentation, data acquisition, and safety features (alarms, etc.). Commercial nickel-based catalyst ground to a particle size of 300-500 μ is being used in the reactor. The catalyst is fluidized using superheated steam, which is also a reactant in the reforming process. The cyclones capture both fine catalyst particles and solid carbon generated by gas phase pyrolysis of the vapors that may occur in competition with the catalytic steam reforming. The Inconel reactor with a porous distribution plate is placed inside a

three zone electric furnace to maintain the reactor at the desired temperature during the endothermic steam reforming operation. The reformed products flow through the spray scrubbers and a cold wall condenser before passing through a coalescing filter to remove aerosols.

Results and Discussion

In the initial tests the pilot-scale fluid-bed pyrolysis reactor was used to produce pyrolysis products from which a slipstream of the product vapors was sent to a 5 cm steam-reforming reactor.^{4,5} The purposes of the run were:

- Shake down the pyrolysis operation in the fluid bed, with emphasis on recent system modifications, demonstrate long duration operation in the pyrolysis mode, and perform online analysis of the product vapors.
- Reform the whole pyrolysis vapors (for the first time) in the 5 cm catalytic steam reforming fluid bed reactor.

The latter was the key objective, since the more chemically stable, lignin-derived phenolics may be more likely to coke on the nickel catalyst. Prior runs in the 5 cm reformer have used only the aqueous carbohydrate-derived fraction of pyrolysis oil. Reforming in the large-scale unit is planned to begin in March 2002 and will be reported at the symposium in June.

The composition of the pyrolysis products from the fluid bed system was unexpected. The char yield for this run was very high (~40%) and is due to multiple reasons: the high ash content, which catalyzes char formation from carbohydrates; and high lignin (32%) and protein (8%) content, both of which produce char yields greater than 30%. Studies in the laboratory showed that, even with small particle size and high temperature, the char yields from peanut shells were a minimum of 25% under conditions where wood char yields would be 12%.

The reforming test proceeded very smoothly. Gas composition at the outlet of the reformer was monitored during the operation and is shown in Figure 2. The composition of the gas indicates that the yield of hydrogen from this agricultural residue feedstock is approximately 90% of maximum. Additional optimization of process conditions should result in somewhat higher yields (note that, in a commercial operation, the remaining CO would be converted to additional hydrogen using conventional water-gas shift processing). In these tests, the gas product stream was flared. No breakthrough of pyrolysis products was noted and the methane level, which is a sensitive indicator of catalyst activity, did not increase. The significant finding here is that the lignin-derived pyrolysis products are reformed completely.

Summary

The steam reforming of biomass pyrolysis oil, when integrated with the production of high value products, is a promising near-term approach to the production of renewable hydrogen. Based on bench-scale work at NREL, a team from Georgia is utilizing the NREL Thermochemical Users Facility and its staff to develop a 10-20 kg/hr scale reactor that will be operated at NREL this year before being run at the production site in Georgia on densified peanut shells. The application in Georgia is at a plant that makes activated carbon from peanut shells and has pyrolysis by-products available for conversion. The key technical goals for the shakedown at NREL are to ensure the safety of the reactor and obtain preliminary performance data on the catalyst, especially physical attrition and deactivation.

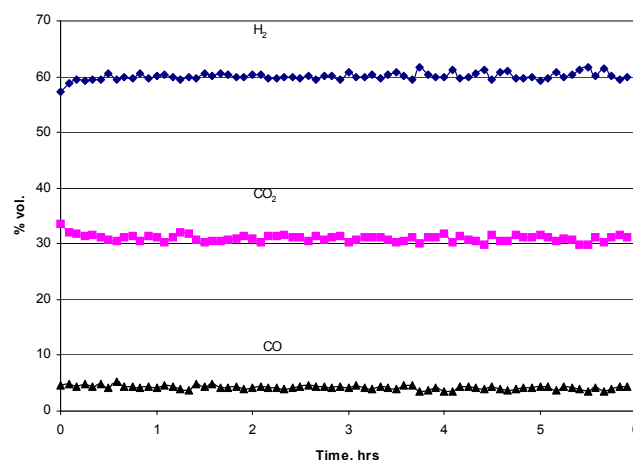


Figure 2. Gas composition from reforming peanut-shell pyrolysis vapors.

In phase two, the reactor will be tested on the pyrolysis vapors produced in the first step of the activated carbon process. An interface system is being designed this year for construction and operation in phase 2. In phase three the hydrogen produced will be purified by converting residual CO to H₂ over a shift catalyst and separating hydrogen from CO₂ using pressure swing adsorption. The purified hydrogen will be mixed with natural gas and used in a transportation demo. Working with the team from Georgia, other agricultural residues and deployment logistics are being evaluated for cost and co-product potential.^{7,8}

The scaled-up reactor will be shipped to the industrial site in Georgia for phase 2 testing in 2002. The hydrogen produced in the third phase of the project will be blended with CNG and used to power a bus in the nearby city of Albany, GA in Phase 3 of this project. This integrated strategy will demonstrate the potential impact of hydrogen and bioenergy on the economic development and diversification of rural areas.

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